PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Catalyst Feeding

We, CELANESE CORPORATION OF AMERICA, of 180 Madison Avenue, New York 16, New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel method and apparatus for feeding a solid powdered catalyst into a reactor, which method and apparatus have been found to be of considerable value in the polymerisation of olefines.

According to the invention, a powdered solid catalyst is fed into a reactor by continuously feeding the catalyst at a controlled rate into a zone provided with a discharge opening communicating with the reactor and continuously feeding a liquid at an independently controlled rate into said zone, said liquid passing through said discharge opening and carrying catalyst therewith as a slurry of controlled solids content into the reactor, a body of the liquid being maintained in the zone referred to and fresh liquid being supplied to the zone at such a rate as to maintain the volume of liquid in the zone between predetermined limits. The catalyst may be fed into the zone below the level of the liquid therein, whereby the surface of the liquid remains relatively undisturbed, so that the volume of liquid in the zone can be controlled by maintaining the level of the liquid within predetermined limits. The volume of liquid in the zone can also be controlled by maintaining within predetermined limits the level of the liquid in a supply tank fed with the liquid and communicating with the zone both above and below the liquid levels in the tank and zone.

As already indicated, the method and apparatus of the invention are of considerable value in the polymerisation of olefines and the invention will be described more particularly in this connection.

In one process for the polymerisation of olefines, especially ethylene, the polymerisation is effected under pressure in a vessel containing a solvent such as cyclohexane or xylene having a solid catalyst comprising a mixture of various oxides suspended therein. In preparing the reaction medium, the catalyst has heretofore been suspended or slurried in the solvent and portions of the slurry have been added to solvent in the reaction vessel as required, the contact time between catalyst and solvent prior to introduction into the reaction vessel averaging several hours.

It has been found that the efficiency of the catalyst, as measured by the weight of polymer produced per unit weight of catalyst consumed, decreases considerably if the catalyst is slurried in the solvent for any length of time before introduction into the reactor. By means of the present invention the catalyst efficiency can be increased by slurrying the catalyst in the solvent and promptly introducing this slurry into the pressurized reaction vessel, the average residence time of catalyst in solvent within the surge tank being a maximum of about 15 minutes and preferably no more than about 60 seconds.

One form of apparatus designed to effect formation of a slurry and transfer thereof by the method of the invention comprises a catalyst hopper for introducing said catalyst into a metering device which discharges into a surge tank. The metering device may be a star-type feeder or a ball or plug valve capable of cyclically operating. Preferably it is a screw conveyor housed within a tube which terminates adjacent the bottom of the surge tank. Catalyst drops from the end of the tube through the surge tank and through a discharge opening into a downcomer extending into the reaction vessel. Solvent is continuously supplied to the surge tank to maintain a predetermined level and passes into the re-

[*Price*

action vessel with the catalyst slurried therein. The inlet to the surge tank is sealed by the metering device and the outlet is sealed by liquid; compressed gas is supplied to the surge tank at a pressure greater than that of the reaction vessel and the difference in pressure permits discharge from the downcomer below the liquid level within the reactor. The rate of feed of the catalyst is determined by the needs of the reactor. Variation in the rate of feed of the solvent thus determines the concentration of the solid catalyst slurried in the solvent during passage to the reactor. A fine mesh screen can be provided to prevent the catalyst from entering any zone wherein it will settle without advancing to the reactor.

The composition of the catalyst will depend upon the nature of the monomer or monomers being reacted and upon the nature of the polymers desired to be produced. In the polymerisation of an olefine such as ethylene, for example, the preferred catalysts comprise those materials disclosed in British Patent No. 790,195, such as metal oxides on a support, e.g. chromium oxide on silica, alumina, mixtures thereof, and the like. The amount of chromium oxide in the catalyst may range from 0.1 to 10 or more weight percent of the support. The preferred support is a silica-alumina composite containing a predominant portion of silica and a minor portion of alumina by weight, e.g. 90—10 silica-alumina. The catalyst, prior to being fed to the reactor, is usually activated with air at a temperature in the range of 750° to 1500° F. for a period of 3 to 10 hours or more. The particle size of the catalyst preferably ranges between about 2 and 200 microns, although smaller particles as well as larger particles of 10 mesh or more can be used.

Monomers which can be polymerised in accordance with the invention include olefines such as ethylene, propylene, 1- and 2-butene, 1- and 2-pentene, 1- and 2-hexene, 1- and 2-octene, 1-dodecene, isobutylene, 2-methyl-1-butene, 3 - methyl - 1 - butene, 4 - methyl - 1-pentene, 4-vinylcyclohexene, 2-methyl-2-butene, cyclohexene, butadiene, isoprene, mixtures thereof. Of these, the preferred monomers are those which give higher molecular weight solid polymers, i.e. 1-olefines of maximum monomer chain length of about 8 carbon atoms and no branching nearer the double bond than the 4-position. Diolefines also produce solid polymers if they have a terminal double bond. In the case of conjugated diolefines, a substituent such as a methyl, chloro- or ethyl group can be closer than the 4-position, e.g. as close as the 3-position to the terminal double bond.

The solvent employed to slurry the catalyst, and in which the polymerisation is preferably effected, is an inert hydrocarbon solvent such as propane, isobutane, n-pentane, isopentane, iso-octane, cyclohexane, methylcyclohexane, decalin, tetralin, benzene, toluene, xylene, mixtures thereof. Of these, cyclohexane is particularly useful.

The temperature of polymerisation normally ranges from about 150° F. to 450° F., with 240° F. to 325° F. being preferred for ethylene and 150° F. being preferred for propylene and higher 1-olefines.

The pressure in the reactor must be high enough to maintain the solvent in the liquid phase and to ensure that monomers not liquefied under the prevailing conditions dissolve in the liquid phase in sufficient amount. This generally requires a pressure of at least 100 to 300 pounds per square inch gauge.

By feeding the catalyst to the reactor in accordance with the invention, the catalyst efficiency is higher and less catalyst is needed to polymerise a given weight of monomer. In addition to the obvious saving due to use of less catalyst, considerable power is saved in separating solid waste catalyst from the polymer solution. The size of equipment for handling solid waste from a plant producing a given weight of polymer will be decreased with attendant savings in equipment cost. Moreover, the increased catalyst efficiency reduces the proportion of catalyst impurities carried into the end product so that an improved product is obtained.

Apparatus embodying the invention is illustrated in the accompanying drawings, wherein

Figure 1 is a schematic view, partially in section and partially in elevation, of an apparatus for introducing catalyst slurry into a pressurized reaction vessel, and

Figure 2 is a schematic view, partially in section and partially in elevation, of another apparatus for forming and feeding a catalyst slurry.

Referring now to Figure 1 of the drawings, there is shown a hopper 11 for containing solid catalyst and provided with a gas-tight removable cover 12. Pressurized inert gas such as nitrogen, argon, or the like, is admitted from a line 13 through gas inlet line 14. A level alarm 15 indicates when additional catalyst must be supplied to the hopper 11.

A discharge spout 16 leads from the hopper 11 to a screw conveyor 17 constructed so that the volume forwarded per turn of the screw decreases from inlet to outlet. To this end, there are provided two screw sections 18 and 19 mounted on a common shaft and driven together by a motor 20, although the same result can be achieved with a single screw section having a downwardly tapered thread portion or a thread wherein the pitch between adjacent turns decreases progressively in downward direction. Solid material passing from screw section 18 is compacted in section 19, to form a gas-tight seal. Screw section 19 is housed within an open-ended tube 21 disposed with a surge tank 22 which is provided with a heating jacket 23. The open end

of tube 21 is aligned with a downcomer 24 in the surge tank 22, discharging into the eye of an agitator 25 below the liquid level within reactor 26. A fine mesh screen 27 of frusto-conical shape, such as wire cloth of about 400 mesh, extends from the top of tank 22 to downcomer 24. The screen 27 is spaced slightly from the end of tube 21 and is open at its apex to direct the flow of solid material from tube 21 to reactor 26. The wire screen 27 prevents solid catalyst from accumulating at the bottom periphery of the surge tank. Moreover, in the event of a sudden increase of pressure in reactor 26, slurry may back up into surge tank 22 but the screen 27 again prevents passage of solid catalyst out of the conical zone defined by the screen. The heated jacket 23 prevents precipitation of dissolved solids from such solvent as might back up into the surge tank under abnormal conditions.

Solvent to slurry the catalyst is supplied to surge tank 22 through a line 28 having a valve 29 which is opened by a level control 30 when the liquid level within the tank 22 drops and approaches the bottom of tube 21. In the event that solvent temporarily fails to leave the tank 22 at the rate it is fed thereto, level control 30 acts on valve 29 to reduce the solvent feed and thus prevent flooding of the tank.

Pressurized gas from line 13 is admitted to screw section 18 through line 31 and, to aid in advancing the materials in opposition to the pressure in the reactor 26, to surge tank 22 through line 32. A control 33 responds to the difference in pressure between the surge tank 22 and the reactor 26. If the pressure is too great, control 33 opens valve 34 to vent gas to the atmosphere. At all other times valve 34 is closed.

Simultaneously with introduction of catalyst slurry into reactor 26, additional solvent is introduced through line 35 and monomer to be polymerised is introduced through line 36. A portion of the reactor contents is continuously withdrawn through line 37 and is treated first to separate unreacted monomer, next to separate waste catalyst and finally to separate the polymer from the solvent in which it is dissolved.

Referring now to Figure 2 of the drawings, a replaceable catalyst receiver 38 delivers catalyst to a catalyst feed tank 39 from whence it drops downwardly through a section of pipe 40 provided externally with an air vibrator 41 to shake loose any adhering catalyst. The catalyst is metered through a star feeder 42 into a conical chamber and then falls through a narrow nipple 43 which extends a short distance into elongated pipe 44, the latter containing a body of solvent 45.

Cool solvent from a line 46 flows through a valve 47 into a solvent tank 48 provided with a level control 49 which regulates the valve 47 so as to maintain a predetermined liquid level in the tank 48 and hence in the pipe 44 which communicates with the tank 48 through a conduit 50. A portion of the cool solvent in line 46 by-passes valve 47 and flows through a line 51 having a small orifice 52 therein to control flow and a valve 53 for fine control of the flow. Line 51 discharges solvent tangentially into pipe 44 at a level just slightly above the bottom of nipple 43 and flushes down into the body of solvent 45 any catalyst on the walls of the pipe 44. Slurry continuously leaves pipe 44 through a narrow conduit 54 to be passed to the reactor (not shown) directly, preferably through the intermediary of an injection pump (not shown).

An inert pressurized gas, such as nitrogen, is admitted through a line 55 to the solvent tank 48 and the pipe 44, at points above the liquid levels therein, and also to the catalyst feed tank 39 and the catalyst receiver 38, so as to prevent contact with air and to equalize the pressure in the system.

If desired, an agitator may be provided near the bottom of the pipe 44 and the liquid outflow from pipe 44 through conduit 54 may be at a higher location than the liquid inflow through conduit 50, but it has been found in practice that the catalyst is adequately slurried in the solvent without such special measures.

The following examples illustrate the invention as applied to the polymerisation of ethylene:—

Example I

Using the apparatus shown in Figure 1, a catalyst comprising chromia on an 86—14 weight percent silica-alumina support, having an overall chromium content of 2.3 weight percent, is dropped from hopper 11 at the rate of 4.2 pounds per hour into screw section 18 and is conveyed thereby into screw section 19 where it is compacted. As the catalyst leaves the bottom of tube 21 it drops into downcomer 24 to pass into reactor 26. At the same time, cyclohexane is admitted to the surge tank 22 at the rate of 416 pounds per hour and also passes out through downcomer 24, being forced out by the nitrogen pressure of 444 pounds per square inch gauge in tank 22. The cyclohexane must pass through screen 27 to leave the surge tank and it mixes with solid catalyst, forming a slurry and flushing the catalyst down. The rate of feed of catalyst and solvent and the size of the surge tank are correlated so that the average residence of catalyst in solvent prior to introduction into the reactor is 5 minutes.

Additional cyclohexane is fed to reactor 26 through line 35 at the rate of 9,130 pounds per hour and ethylene is introduced through line 36 at the rate of 1,380 pounds per hour. The reactor is operated at a temperature of 280° F. and a pressure of 420 pounds per square inch gauge. Slurry is continuously withdrawn from the reactor through line 37, is throttled to flash off unpolymerised ethylene, is centrifuged to separate catalyst and is

agitated with water to precipitate polyethylene.

EXAMPLE II

Using the apparatus shown in Figure 2, the same catalyst as in Example I is fed to pipe 44 at the rate of 4 pounds per hour and cyclohexane is fed at the rate of 0.8 gallons per minute through conduit 50 and at the rate of 0.2 gallon per minute through line 51, slurry continuously discharging through conduit 54. The residence time of slurry in pipe 44 is about 10 seconds and the residence time from leaving pipe 44 until the slurry enters the reactor is about 30 seconds. The reactor operates as set forth in Example I.

WHAT WE CLAIM IS:—

1. Method of feeding a powdered solid catalyst into a reactor, which comprises continuously feeding the catalyst at a controlled rate into a zone provided with a discharge opening communicating with the reactor and continuously feeding a liquid at an independently controlled rate into said zone, said liquid passing through said discharge opening and carrying catalyst therewith as a slurry of controlled solids content into the reactor, a body of said liquid being maintained in said zone and fresh liquid being supplied to said zone at such a rate as to maintain the volume of liquid in said zone between predetermined limits.

2. Method according to Claim 1, wherein the catalyst is fed into said zone below the level of the liquid therein and said level is maintained within predetermined limits.

3. Method according to Claim 2, wherein said ctalyst is fed into said zone through a passageway terminating below the level of liquid therein and is caused to form a plug at the outlet from said passageway.

4. Method according to Claim 1 and comprising maintaining within predetermined limits the level of said liquid in a supply tank fed with said liquid and communicating with said zone both above and below the liquid levels in said tank and zone.

5. Method according to any of the preceding claims, wherein an inert gas is maintained under pressure over the liquid in said zone and the slurried catalyst is forced from said zone by the pressure of inert gas.

6. Method of feeding a powdered solid catalyst into a reactor, substantially as hereinbefore described.

7. Process for the manufacture of a polymer of an olefine by polymerisation thereof in a solvent for the olefine and its polymer in presence of a solid catalyst slurried in said solvent, wherein the ctalyst is supplied to the vessel in which the polymerisation is effected by the method claimed in any of the preceding claims and the contents of said vessel are withdrawn in a measure as olefine and fresh catalyst slurry are supplied thereto.

8. Process according to Claim 7, wherein the olefine polymerised is ethylene and the average time of contact of the catalyst and liquid in the zone into which they are introduced for slurrying is not more than 15 minutes.

9. Process according to Claim 7 or 8, wherein a thermally activated chromium oxide-silica-alumina catalyst is employed.

10. Process for the polymerisation of ethylene, substantially as described in the Examples.

11. Polyolefines whenever produced by any of the processes claimed in Claims 7 to 10.

12. Apparatus for feeding a powdered solid catalyst into a reactor as a slurry of controlled solids content, comprising a reactor, a vessel provided adjacent its bottom with a discharge opening communicating with said reactor, means for continuously supplying a solid catalyst to said vessel at a controlled rate, means for continuously supplying to said vessel at an independently controlled rate a liquid in which said catalyst is to be slurried, said liquid passing out through said discharge opening with said solid catalyst slurried therein, and means for maintaining within predetermined limits a head of liquid in said vessel.

13. Apparatus according to Claim 12 and comprising a pipe for introducing the catalyst into said vessel, said pipe opening below the normal liquid level therein.

14. Apparatus according to Claim 13 and comprising a screw conveyor operating within said pipe, said screw being adapted to forward the catalyst through the pipe at a lower rate near the outlet thereof than at the inlet so as to cause the catalyst to form a plug sealing said outlet against ingress of liquid from said vessel.

15. Apparatus according to Claim 12, wherein said means for maintaining within predetermined limits a head of liquid in said vessel comprises a supply tank, means for feeding said liquid to said tank and means for maintaining the level of liquid within the tank between predetermined limits, and conduits connecting said vessel and tank both above and below the normal liquid level therein.

16. Apparatus according to any of Claims 12 to 15 and comprising means for maintaining a superatmospheric pressure of gas over the liquid in said vessel.

17. Apparatus for use in polymerising olefines, substantially as shown in and described with reference to Figure 1 of the accompanying drawings.

18. Apparatus for feeding a powdered solid catalyst at a controlled rate into a reactor and suitable for use in polymerising olefines, substantially as shown in and described with

reference to Figure 2 of the accompanying drawings.

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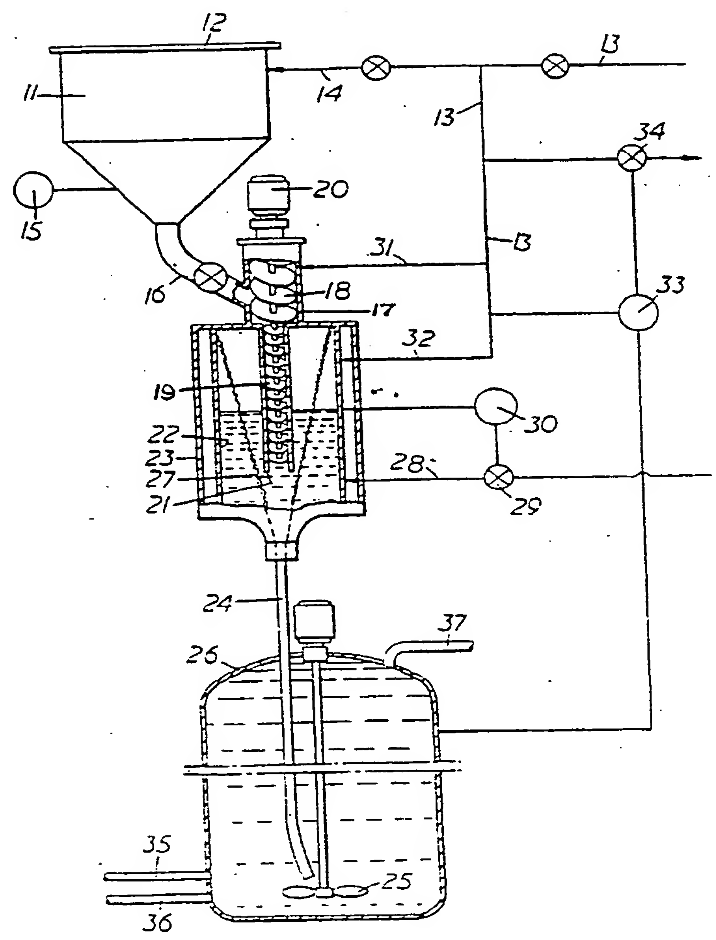
FIG. 1.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Sheets 1 & 2

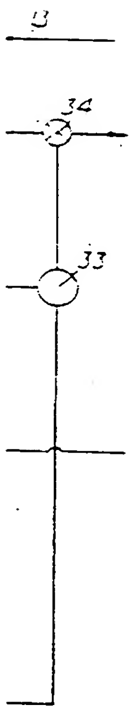

FIG. 2

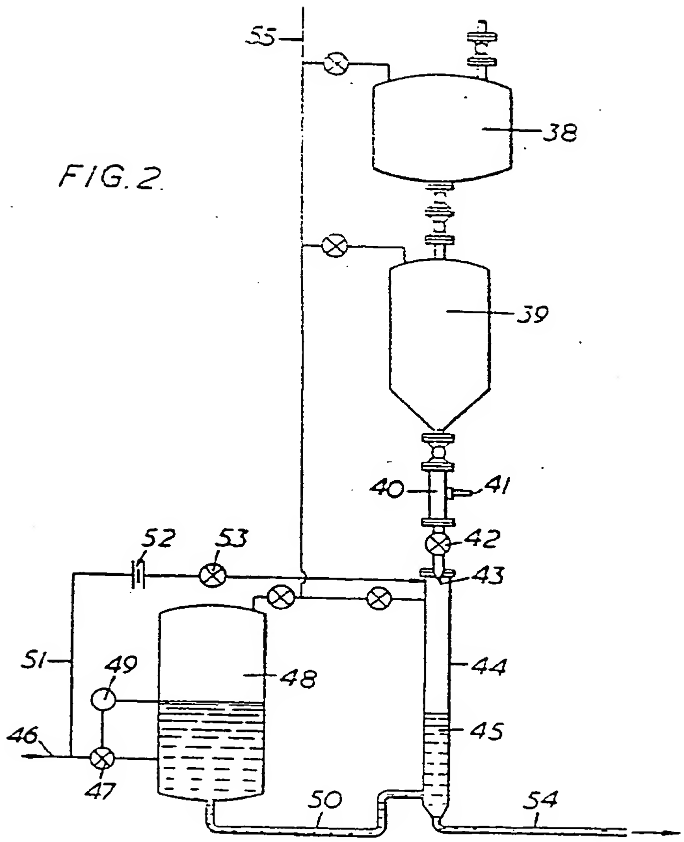

FIG. 1

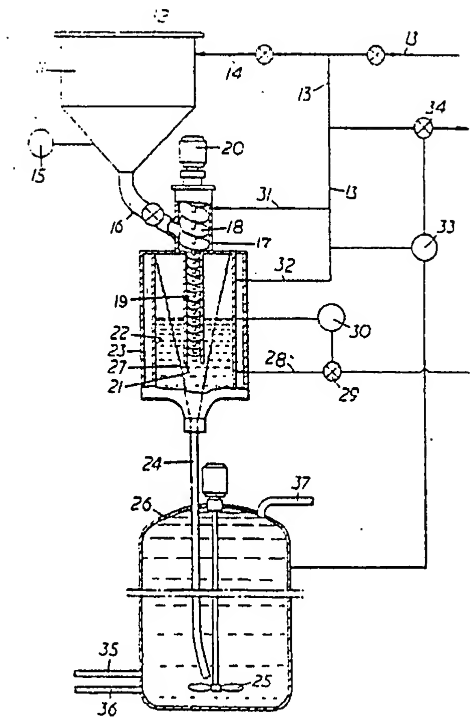
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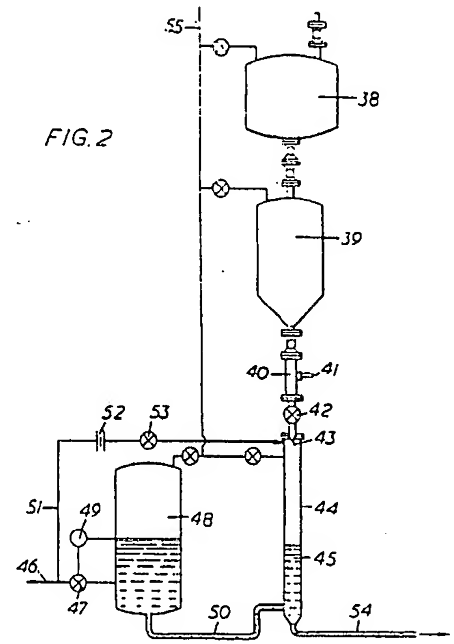
FIG. 2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